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Review Article

# Zirconia in dental prosthetics: a literature review

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ABSTRACT

A large portion of the global human population carries a type of medical implant. Dental implants are an important part of this category, and the crowns they support are vital for satisfying the patients' needs both functionally and aesthetically. Materials science pertaining to dental crowns is a driver of their development, and currently zirconium oxide (zirconia) is a promising non-metal alternative, exhibiting biocompatibility and excellent mechanical and aesthetic properties. This review aims to collate a selection of the extensive testing and research that has been performed and evaluated on a variety of zirconia-based ceramics, as there are many commercial brands developing blank and powdered samples for refinement into structurally sound dental prosthetics. Significant advancements regarding manufacturing technologies for zirconia-based ceramics are also currently in progress. Methodologies and conditions for uniaxial and isostatic pressing of zirconia powder are reviewed, as are the benefits of emerging CAD/CAM technologies. Several knowledge gaps were identified based on this review, primarily that different sintering conditions and methodologies, such as two-step sintering, should be investigated experimentally. Preliminary studies using alternative methods show promising results, and further trialling would help to ensure that the mechanical, aesthetic and ageing properties of the final product are enhanced and optimised.



**Elsa Antunes** obtained her PhD degree in Chemical Engineering from James Cook University in 2017. Elsa's PhD was focused on understanding the impact of microwave pyrolysis conditions on biochar properties produced from diverse biomass sources. In 2018, she joined James Cook University as a Lecturer in Mechanical Engineering. She is currently focused in materials engineering, such as biomedical implants, transparent ceramics and surface functionality of biochar for water purification, resource recovery and desalination.

## 1. Significance of biomedical implants

When the term biomedical implant is used, it is generally referring to a device used to support or replace a fraction of the whole biological structure [1], either for short or long-term use. Procedures involving such implantations are common, with millions of patients undertaking them each year to improve their quality of life [1]. In fact, experts estimate that 1 in 17 people in industrialised countries carry an implanted device of some form [2,3]. The past six decades have seen major advancements in the areas of microelectronics, biotechnology, and materials science [3]. This has facilitated rapid develop-

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ment of implant technologies in all medical fields, for example in the areas of orthopaedics, dentistry, and ophthalmic and cardiovascular health [1].

### 1.1. ARGMD classifications

The extent to which a medical device is relied upon by its carrier for supporting or sustaining life varies depending on its purpose. The Australian Regulatory Guidelines for Medical Devices (ARGMD), administered by the Australian Government Department of Therapeutic Good Administration, categorises medical devices into three major classes (I, II or III). This is to ensure that these devices are regulated in accordance with the risks they pose individually [4].

Class I devices are considered low to medium risk in terms of the potential for harm to be inflicted on the patient [4]. They are generally not intended to sustain life, are non-medical and usually for transient (less than 60 min) or short-term use. They are also non-invasive, meaning they either do not touch the skin or only contact intact skin. Examples of Class I devices include plaster or elastic bandages and non-sterile dressings [1,4].

Class II devices present a risk level ranging from medium to high [4]. They can be invasive, meaning the device penetrates the body through an orifice or is inserted during surgery. They are non-active (do not require a power source), and are usually for short term use with the exception of implants in the oral or nasal cavities and the ear canal, as these are often long-term. Examples of Class II devices include contact lenses, implantable joint replacements, and dental prostheses such as bridges and crowns [4].

Class III devices are considered to impose a high level of risk of harm on patients [4]. These devices/implants are usually invasive, and are generally required for applications involving the circulatory and central nervous systems. This means they are most commonly for long-term use; however, Class III devices can also be transient/short-term depending on factors such as whether it is to be absorbed by the body, and whether it is intended to cause biological change. Examples of Class III devices include absorbable sutures, cardiovascular catheters and antibiotic bone cements [4].

### 1.2. Drivers for development in prosthodontics

Most dental prosthetics are Class II devices according to the ARGMD as they are usually non-active but invasive and intended for long-term use [4]. Prosthodontics is a specialised branch of dentistry that focusses on the design, manufacture and fitting of these artificial replacements for teeth, as well as restorations of natural teeth. This field of dentistry holds great significance as there is often a fine line between patient satisfaction and dissatisfaction due to the precision required for the prostheses. Nevertheless, it is understood that the patients' chief complaints belong to one or multiple of the following categories: comfort, function, social, and appearance [5].

Lack of comfort is generally the main source of urgency if a dental prosthetic is required. For example, a condition such as gingivitis, which is an inflammation of the gingival complex, will cause sensitivity, swelling and pain in the gums. If left untreated, it will begin to affect the underlying bone and can eventually cause the teeth to loosen, a condition known as periodontitis [6]. Conditions such as the two aforementioned are common, and the percentage of population with decayed or missing teeth is particularly high in Australia [7]. Fractures of the teeth due to events such as force of collisions may also cause pain because of the exposure and displacement of the tooth's soft inner tissue known as the dental pulp [8]. Therefore, it is apparent that in the structural restoration of the tooth via artificial implantation, prosthodontics also aims to alleviate pain and discomfort for the patient.

To compound the physical pain caused by gum disease and tooth loss, the ability for patients to perform some everyday activities is often also compromised. A 2012 study was conducted to compare the production of certain speech sounds by patients with and without anterior teeth [9]. One conclusion of these studies was that the use of partial dental prostheses was beneficial in improving speech [9]. Dental prosthetics also make it easier for patients with gum diseases to eat without feeling excessive pain, by filling the gaps where teeth have fallen out and protecting the inflamed gums as the patient chews. These are evidence to suggest that prosthodontics also allows patients suffering tooth loss to live a more functional life.

In advanced stages of a periodontal disease, the supporting bone and tissue are destroyed, and plaque and tartar build-up cause the gums to swell and pull away from the tooth. This causes pockets between the gum and the teeth, and the presence of bacteria that inhabit this space causes an often-powerful odour to be expelled into the mouth. This is especially severe if the cavity is not sealed well from the mouth air [10]. Conditions with these symptoms will also leave a foul taste in the patient's mouth. These symptoms are often awkward and embarrassing for patients during social interactions. Properly installed dental implants for the treatment of such conditions are also an established way to restore confidence for the patient in their social endeavours.

The final factor that motivates patients to seek prosthodontic help is the desire to improve appearance. Missing teeth, especially the more visible incisors and canines, is widely perceived as being aesthetically unappealing. A study conducted by the University of Groningen Dental School evaluated the personal aesthetic perceptions of 74 patients with varying degrees of teeth missing (e.g. incisors, pre-molars, etc.) against patients with a natural dentition. In terms of positive feelings, on a scale of 0–5 (0 being feelings not present, and 5 being feelings strongly present), the average score by those missing incisors was 1.0. This was compared to an average of 2.6 by those missing no teeth [11]. Whilst this study was conducted in 1989, it can be assumed that with the increased levels of employment competitiveness as well as the greater emphasis in the media on personal appearance, these negative perceptions have only become more pronounced. Appropriate dental prosthetics in terms of colour, shape and size are the most common solution for patients who feel burdened aesthetically by a lack of a complete dentition.

## 2. Conventional prosthodontics

### 2.1. Common materials for foundation components

It is of paramount importance that these implants be not only functional, but capable of enduring for their anticipated useful life. In the case of fixed dental prosthetics (FDPs), namely crowns (single prosthetic), bridges (several joined prosthetics) and dentures (full upper or lower jaw prosthetics), the aim is to maximise this lifespan. This is desirable not only to avoid premature failure of the implant, but also to avoid usually costly and often impractical secondary removal surgery [2].

In this field, the crown or bridge is referred to as the prosthesis and is supported by several foundation components used to fix it in place for long term functionality. In the cases of fixed partial or complete dentures, the implant is considered to be the implant post that is screwed into the alveolar bone. This component houses an abutment, which is a threaded sleeve that allows for the attachment of the prosthesis itself (i.e. crown, bridge, denture etc.). The implant posts are generally pure titanium (Grade 1–4) or a titanium alloy. The system titanium-aluminium-vanadium, also known as Ti-6Al-4V (Grade 23), is a commonly used alloy for this application due to its higher hardness and better resistance to fatigue when compared to commercially pure titanium [12,13].

Whilst the implant post itself is usually titanium due to its superior machinability which is required for precision threads, the abutment material is selected with added aesthetic factors in mind. Due to the translucency of some common materials used to make dental crowns, ceramic abutments are attracting increasing amounts of attention. This is not only because of their similar colouration to that of a natural tooth, but also for their superior strength and fracture toughness when compared to metallic alternatives such as pure titanium, and chrome-cobalt, dental gold and titanium alloys [14,15]. To bond the crown or bridge to the abutment(s), the most common technique is to use a luting agent known as a dental cement. Ideally, the cement should be durable, provide good adherence to natural and restorative materials, be non-toxic, have adequate strength and low solubility [5]. Whilst no variant exists that meets all the criteria, the most commonly used cement is zinc phosphate. Its only limitation is in its biocompatibility; however, these are well documented. Alternative cements include zinc polycarboxylate, glass ionomer and resin-modified glass ionomer [5].

### 2.2. Mechanical, aesthetic and aging properties

While the foundation components of the prosthetic are crucial to ensure longevity and comfort, the crown forms the outer layer of the structure. This not only means that it is the most aesthetically influential component, but because of its exposure to the external environment of the mouth, the conditions it must endure are somewhat harsher than that of the internal components. Regarding mechanical properties, flexural strength quantifies the ultimate stress required to fracture or plastically deform the specimen [16]. The prosthesis must exhibit good flexural strength to withstand the often eccentric axial masticatory force on the tooth, which studies have quantified at maximum values in excess of 1200 Newtons (N) in extreme cases [16,17]. Fracture toughness is also a critical factor of clinical reliability, as it needs to be high enough to resist the rapid propagation of any flaws that may form [16]. For dental applications, this property is commonly tested using the indentation fracture toughness technique (IF) [16]. Density plays a key role is ensuring homogeneity in the material, and it is a common goal of experimentation with ceramics manufacture to optimise this property. Higher densities correlate to lower porosity and thus higher hardness and fracture strength, both desirable characteristics of dental prosthetics. Hardness is commonly quantified via microhardness tests using instruments such as Knoop or Vickers diamond indenters [16].

In line with the necessity for the patient to be satisfied with the appearance of the prosthetics, aesthetic properties, primarily colour and translucency, must be optimised. Correctly matching the colours and contours of adjacent teeth is often vital in maintaining patient satisfaction [5]. While advancements in technology have increased the effectiveness of colour matching instruments such as spectrophotometers, colorimeters and digital cameras, ultimately it is the material of the crown itself that will set the colour limitations [5,18]. Ceramics have a much more tooth-like natural colouration compared to metals [19]. Translucency, which is a property describing the level of light permitted and diffused through the object, is emphasised as a primary factor for dictating aesthetic outcome [20]. This is mainly applicable to ceramic restorations, considering metals are opaque. Correctly matching the translucency of the natural tooth structure is crucial, and is dependent on a variety of factors such as material and thickness, with thinner-walled crowns exhibiting higher translucency in general [5,20].

Whilst there are benchmark values for every mechanical and aesthetic parameter, it is inevitable that, over time in use, these properties will degrade. This is known as hydrothermal ageing or low temperature degradation (LTD) and is detrimental to the application of the material [21,22]. LTD is not fully understood, though some believe it to be caused by the humidity of the oral environment which can cause stress corrosion in certain materials [23]. Others hypothesize it to be the result of residual stresses resulting from the presence of water vapour [24]. Regarding metals such as titanium, LTD is not a significant issue due to the oxide film that forms on these prosthetics, making them highly resistant to corrosion in the oral environment [25]. In comparison, LTD is very common in dental ceramics, and aging is considered a serious limitation for these materials [21]. It must be noted that the ageing and degradation of any prosthetic material can be accelerated by a number of other factors, such as gingival conditions, implant geometries and loading cases, smoking and oral hygiene [25]. Therefore, with the intended long-term use of a fixed dental prosthetic, ageing properties play a large role in deeming a material fit for application.

### 2.3. Common ceramics materials for dental prostheses

All-ceramic and metal-ceramic crowns are becoming a more attractive option for patients, especially for anterior tooth restorations. This is mainly due to their good mimicking of the optical and aesthetic properties of natural enamel and dentine, with no sacrifices to biocompatibility or chemical durability [19,26]. Porcelain-fused-to-metal (PFM) restorations have been the most common metal-ceramic option for over 50 years [27]. Aesthetically, whilst porcelain is naturally solid white in colour, the fused metallic collar placed on the margins of the crown is often described as a "black line" by patients with gingival recession [28,29]. This is often not deal for those seeking a natural looking prosthetic. The translucency of porcelain is also inconsistent, as it relies heavily on the scattering of light, which in turn is dependent on factors such as crystal content and particle size [28,30]. This makes for complex manufacture to achieve satisfactory results. The fracture toughness of a PFM crown with 0.3 vol fraction of leucite is approximately 1.10 MPa $m^{1/2}$ [31], which is satisfactory for most applications. The flexural strength varies depending on the type of metal used as the substructure to strengthen it, as unreinforced feldspathic porcelain sees low values of 55–65 MPa [32].

Of the all-ceramic prosthetic materials, zirconium oxide ($ZrO_2$ – zirconia) as a base material has shown great promise. This is not only due to its excellent mechanical properties, but also due to a unique phenomenon known as transformation toughening, first reported in 1975 [33]. This attribute sets it apart from other usually brittle ceramics in that, at room temperature, pure zirconia exhibits a monoclinic (*m*) crystal structure, and when heated to 1170 °C it transforms to a tetragonal (*t*) structure [34]. There is also a third cubic phase (*f*) that occurs between 2370 °C and melting point [34]. Upon cooling, the $t \rightarrow m$ transformation induces an approximate 4.5% volume increase which could produce catastrophic failure, so it is typical to stabilize the zirconia with oxides such as magnesia (MgO), yttria ($Y_2O_3$), cerium oxide ($CeO_2$) and calcium oxide (CaO) [34,35]. This controls the stress, allows the more stable tetragonal structure to be present at room temperature, and also slows or halts crack propagation due to a $t \rightarrow m$ transformation local to the crack tip [34–36].

Yttria is the most established and well documented dopant for inducing transformation toughening. Its addition in Yttria-stabilised tetragonal zirconia polycrystal (Y-TZP) decreases the driving force of the $t \rightarrow m$ transformation and hence its temperature [21]. This makes it possible for the metastable tetragonal phase to be retained at room temperature, assuming the yttria content is above 2 mol% [21]. The $ZrO_2$-$Y_2O_3$ phase diagram shows the temperatures at which these phases are present as yttria content is varied [21].

In order to produce a composite that is wear resistant with higher fracture toughness and strength relative to its individual monolithic forms, the zirconium oxide matrix can be toughened with alumina particles to form Alumina Toughened Zirconia (ATZ) [37]. Mechanical properties are dependent not only on the ratio of alumina to zirconia, but also on the dopants used to stabilize each. This makes this composite quite versatile in terms of its applications. A study, performed in 2009, used Baikalox SM8 alumina and 3Y-TZP shows the change in hardness and fracture toughness as the proportions are altered. The conditions under which these results were obtained was uniaxial pressing under 50 MPa followed by 1500 °C conventional sintering for 2 h [37].

This study drew many notable conclusions about ATZ, the optimal composition for dental application was 20 wt% alumina, corresponding to the maximum fracture toughness of approximately 7.45 MPa $m^{1/2}$ and a Vickers hardness of 16.05 GPa. The increased fracture toughness relative to the individual monolithic materials was owed to the inhibition of grain growth of the alumina by the addition of zirconia. Aesthetically, ATZ performs very well as both zirconia and alumina are naturally white, and the composite can be processed to a good surface finish. However, the introduction of alumina reduces overall translucency, and this may not be ideal in certain applications [38]. In terms of aging, the doping of alumina as low as 0.25 wt% to zirconia-based ceramics (yttrium partially stabilised) is known to improve the resistance of the material to LTD [38]. It does so by limiting the amount of tetragonal grain growth during sintering, resulting in a more stable structure [39]. Overall, ATZ exhibits the highest flexural strength of any known ceramic, with values ranging from 1800 to 2400 MPa at room temperature [38]. Due to its relatively good resistance to aging, high strength and aesthetic limitations, it shows the most promise for orthopaedic implants or posterior FDPs.

There are currently many options available for commercially monolithic zirconium oxide materials. Not only is the market size for dental implants growing annually and expected to continue increasing, but the proportion of these implants made of monolithic zirconia is also forecast to grow. This is evidenced in models analysing historical and forecast market growth for dental implants in the U.S, which project the proportion of the total dental implant market made up by zirconia implants to almost double by 2024 [40]. It must be noted that these models analyse the market trends for the implants themselves, rather than the supported prosthetic, though are useful to highlight the increasing confidence in zirconia for dental applications due to advancing technology.

Monolithic zirconia variants are generally favourable over ATZ due to the lack of alumina present to lower the translucency. Y-TZP is the most common of these, with the doping of yttria for the purpose of retaining a tetragonal crystal structure, as has previously been explained. A common biomedical grade is 3 mol% yttria (3Y-TZP) [36]. This is readily available as raw (green) powder, pre-sintered blanks that can be soft-machined then sintered, or fully sintered blanks that require hard-machining. Whilst it is a longer process, the pre-sintered blanks are generally a more reliable option, as hard-machining of fully sintered blanks can cause a $t \rightarrow m$ transformation on the surface, leading to microcracks and quicker LTD [41]. CeramTec is a company that manufacture pre-sintered zirconia blanks with diverse compositions and properties.

CeramTec blanks are manufactured using a combination of uniaxial and hot isostatic pressing, and pressureless (conventional) sintering, with sintering temperature specified to be 1450 °C [42]. It is observed that the flexural strengths of all variants are substantially lower than those stated in literature for ATZ. This can partially be attributed to the low proportions of alumina ($Al_2O_3$). Flexural strength is seen to range from 840 to 1200 MPa and to grow with alumina content whilst translucency diminishes. These values generally align with those presented in literature, though some experiments report lower values due to influences of polishing and chosen shade of the ceramic [41,43]. Mechanical properties of 3Y-TZP are not only dependent on composition, but also on grain size which is dictated by sintering parameters (mainly, time and temperature). As temperature and duration of sintering increases, so too does the grain size. Above a grain size of 1 $\mu$m, 3Y-TZP is more vulnerable to spontaneous $t \rightarrow m$ transformation which can result in failure; below a grain size of 0.2 $\mu$m, the material loses its transformation toughening attribute and fracture toughness therefore diminishes [38]. In line with this, another study concluded that the critical grain size to retain the $t$ phase is between 0.2 $\mu$m and 0.6 $\mu$m, depending on yttria content [44]. A study, performed in 2007, using a specimen of similar composition to those offered by CeramTec showed the variation of fracture strength, a good indicator of fracture toughness, with grain size. This study concluded that a grain size of 380 nm (0.38 $\mu$m) maximizes fracture strength [45].

Just as in ATZ, the CeramTec products are purposefully doped with trace amounts of alumina to decelerate LTD. It is important to note that increased amounts of alumina do not necessarily correlate to higher resistance to LTD; rather the optimal doping proportion for 3Y-TZP is widely agreed to be 0.25 wt% [46]. This again varies according to sintering conditions. It gives merit to the notion that the monolithic zirconia form, whilst inferior in terms of flexural strength, is not severely disadvantaged in terms of its resistance to hydrothermal degradation in comparison to its composite form. A 2015 study confirmed this for sintering temperatures of 1450 °C and 1550 °C, with both experiments confirming that the Zpex 3Y-TZP specimen (300 MPa cold isostatic pressed) with 0.25 wt% alumina took longer to degrade than with 5 wt% alumina [47]. This was based on vol% of unstable monoclinic phase in the specimen after 40 h of simulated hydrothermal treatment.

It should be noted that experiments have been performed to assess the feasibility of TZP specimens with higher yttria content (e.g. 4Y-TZP). These experiments concluded that 4Y samples had a higher resistance to hydrothermal ageing when compared to lower yttria content, quantifiable by the lower fraction of unstable monoclinic phase over time [48]. Whilst this is ideal, the advantages are negated by the increase in average grain size [48] and substantial decrease in fracture toughness [47] as yttria content is increased. For this reason, 3 mol% yttria is widely considered to be the optimal dopant content to balance aging and mechanical properties.

## 3. Manufacturing technologies for all-ceramic dental implants

Before the sintering process can take place, a procedure of forming and shaping must be undertaken for ceramics. This is achieved using a combination of moulding, compaction and in some cases heat to produce a ceramic body with the desired shape and size. The aim is to increase the solid content in the material to the highest possible level during compaction, which means minimising or at least regulating pore size and frequency [49]. Pores, which are voids in the microstructure of the material, have been experimented with using zirconia, and the results showed a decrease in both elastic modulus (stiffness) and hardness of the material as pore content increased [50]. It is therefore not ideal for dental ceramics, which require intermediate hardness and high stiffness as evidenced, to have a high porosity. Three traditionally used techniques for ceramic powder, particularly zirconia, are uniaxial compaction (dry pressing) and cold or hot isostatic compaction. While the general cost to manufacture using each of these techniques can be commented on, it is important to note that cost is dependent on many factors beyond the technique itself. These include the level of expertise available at the place of manufacture, the level of detail required for the product, and the machinery/tooling brands available to the technician. For example, it is generally accepted that hot isostatic pressing is the most expensive technique to manufacture zirconia products, due to increased cycle times and higher running costs. However, depending on the degree to which the manufacturer has refined the cycle parameters, cycle times for this technique may be reduced sufficiently to offset these additional costs and make it more cost-effective relative to the alternatives. Such refinements are currently being explored to make these higher-quality products more accessible to the average consumer.

### 3.1. *Dry pressing*

Dry pressing is a process of uniaxial compaction of the ceramic powder via means of hydraulically operated upper and (occasionally) lower punches. In dental ceramics, this technology is beginning to age with access to isostatic pressing becoming easier. In green state zirconia (i.e. raw, non-sintered zirconia powder), this method is known to create density heterogeneities which makes for inconsistent mechanical properties throughout the blank [51]. This makes dry pressing unsuitable for larger pieces such as bridges, where the density irregularities will be more pronounced; however, it is still often viable for single crowns [51]. The Weibull modulus is a widely accepted parameter to describe the structural reliability of brittle dental ceramics such as zirconia [52]. It takes into account a variety of factors, such as the probability of failure and the fracture strength [53]. Lower Weibull modulus correspond to a more frequent presence of microstructural flaws and defects, which lead to a lower reliability [52]. The Weibull modulus for uniaxially pressed 3Y-TZP blanks, based on limited literature, is usually approximately 5 (using a 3-point flexural test), and is therefore is low relative to other methods [54]. The main advantage of dry pressing is the comparatively low equipment and running costs. Also, in many cases it can produce more precise shapes resulting in less required post milling and therefore less wastage of material [51]. For this reason, it is common to use dry pressing as a pre-processing phase to obtain shape, before isostatic pressing ensures homogeneity. Due to the decreased use of this shaping method, there is not a wide range of previous studies to validate conventional parameters; however, the few that are available confirm a recommended uniaxial compaction pressure of 150–200 MPa for 3Y-TZP powder [46,49].

### 3.2. *Cold isostatic pressing*

Cold Isostatic Pressing (CIP) makes use of a high-pressure fluid chamber to compact ceramic powder that is contained inside a flexible mold. Isostatic pressing in general is much more comprehensive in terms of ensuring high and homogeneous density (i.e. less porosity) throughout the zirconia blank

[51,53,55]. This high uniformity yields mechanically stronger blanks when compared to uniaxial pressing, and makes for an easier and more effective sintering process [55]. Literature shows that the mean Weibull modulus for CIP blanks with composition and characteristics alike CeramTec blanks ranges from 6 to 8 based on a 3-point flexural test [53,54]. However, the shapes produced are often not as precise, and the extra milling required to refine the product to a satisfactory level causes uneconomical material wastage [51]. Compaction pressure for CIP is cited in literature as 300 MPa, though this can be altered to as high as 1000 MPa if required [56,57].

### 3.3. *Hot isostatic pressing*

The concept of Hot Isostatic Pressing (HIP) is similar to that of CIP, though it makes use of pressurised and heated inert gases such as argon rather than room temperature fluid. This is often not only a forming process, but a finishing process as well, since the result can be a fully sintered product. The process takes place in a furnace, with the container to shape the powder being made of a high-melting point sheet metal. HIP is advantageous in that it produces the highest density products with isotropic (direction-independent) properties; however, its main disadvantage comes in the high costs associated with both the initial investment and the general running costs due to heating. To compound this, products of HIP are much harder relative to CIP and dry pressing, meaning the final shape can only be refined using heavy milling techniques, further increasing overall cost. In terms of the mechanical properties achievable using HIP, virtually fully dense 3Y-TZP blanks have been obtained, having a porosity of less than 0.15%. Mechanical properties are seen to vary vastly with temperature for HIP [58]. Fracture toughness values as high as 1600 MPa, and Weibull modulus in excess of 10.6 (based on 3-point flexural test) have been achieved for fully dense blanks [58]. Fully dense HIPed blanks can have grain sizes of 0.36 $\mu$m or less and can resist LTD in harsh hydrothermal environments, though the more typical results (94.5% density, 0.6 $\mu$m or less grain size) resisted aging in air for 2000 h [58]. Conventionally, HIP temperature and pressure ranges from 1300 °C–1600 °C and 140 MPa–150 MPa respectively, and the process duration is usually 1 h [58,59].

### 3.4. *CAD/CAM technology*

Evidence from both materials development and long-term clinical studies strongly suggest promise for the field of CAD/CAM (Computer-Aided Design/Manufacturing) as a future trend in dental ceramics. This subtractive manufacturing technology allows the technician to prepare the tooth restoration model in software, and relay the information to a computer assisted processing machine for milling from a blank [60]. The CAD/CAM methodology has many advantages in comparison to traditional physical impression-making. Time to fabricate is much lower and less prone to human error [60]. Measurements and fabrication are also very precise and thus final quality is high [60]. In fact, CAM zirconia with no other surface treatment (i.e. polishing, sandblasting etc.) has been experimented with to have a characteristic flexure strength of approximately 821 MPa [61]. This is promising when considering the surface damage imparted on the sample by the milling procedure. Currently the only disadvantages come in the financial viability of these systems, with the initial investment being quite high [60].

An important characteristic of a successful dental restoration is marginal adaptation. This essentially describes the degree to which the prosthesis matches the surrounding teeth dimensionally. Inadequate marginal adaptation leads to plaque accumulation, which in turn can cause microleakage (i.e. infiltration of bacteria), as well as endodontic inflammation and periodontal diseases [62]. CAD/CAM technology, which is reliant on dimensional predictions that account for shrinkage during sintering, has demonstrated an improvement in marginal adaptation of dental zirconia prosthetics [63,64]. Some CAM systems can produce a marginal discrepancy as low as 9 $\mu$m (prior to cementation) [63], which is well below the widely accepted limit of 120 $\mu$m [62]. This is additional evidence to suggest that the use of CAD/CAM will further streamline the dental ceramic fabrication process and provide more reliability for the patient.

## 4. Sintering of zirconia dental prosthetics

As has been evidenced, characteristics such as flexural strength and resistance to LTD are largely dependent on grain size for polycrystalline materials such as zirconia. The sintering process has a direct influence on the resultant grain growth rate, which, if too high, will begin to adversely affect flexural strength and will make it difficult to obtain high density [45,65]. Crystalline content in ceramics is also known to dictate translucency [66], and a study performed in 2013 using various 3Y-TZP blanks concluded that high translucency in the products corresponded to smaller grain sizes and shorter sintering times [67]. As such, conventional sintering techniques are being challenged by new innovations that aim to optimise key parameters such as temperature, heat rate, and sintering (dwelling) time.

### 4.1. *Conventional sintering*

The conventional sintering process consists of heating a pre-compacted blank in a high-temperature furnace to densify the product. The pivotal parameters with this technique are dwelling time, maximum furnace temperature and heat rate supplied to reach the maximum temperature. A study performed in 2013 used conventional sintering to evaluate the effect of sintering temperature on flexural strength and grain size. It used Ceramill ZI Y-TZP blanks, maximum sintering temperatures ranging from 1300 °C to 1700 °C, a heat rate of 8 °C/min and a duration of 120 min. It ultimately concluded that conventional sintering was optimal in terms of flexural strength (1100 MPa–1250 MPa) for sintering temperatures ranging from 1400 °C to 1550 °C [66]. Another study conducted in 2008 used conventional sintering between 1100 °C and 1500 °C for Zpex 3Y-TZP for a duration of 1 min at a heat rate of 5 °C/min. This was to measure the relation between density and grain size. It concluded that the optimal grain size to give the highest density (98.8%) was 275 nm [68]. It also found that as temperature was increased, whilst densification was marginal, grain growth rate was high which makes controlling the process difficult [68].

These results are confirmed by another investigation into conventional sintering conducted in 2012, also using Zpex blanks. It found an average grain size of approximately 256 nm with 98.3% density at a sintering temperature of 1400 °C [69]; though the dwelling time was much longer at 60 min making for a more uniform material. From the literature available, it is apparent that conventional sintering can achieve grain sizes that produce desirable mechanical and optical properties. However, the high temperatures required lead to fast grain growth which could damage quality consistency.

### 4.2. Two-step sintering

Initially developed in the 1990's by Chu et al. [70], with subsequent refinements by Chen and Wang [71], the two-step sintering process (TSS-CW) has become widely used. It consists of high temperature heating to T1 °C followed by sustained structural freezing to T2 °C, and was claimed to achieve densification with no grain growth within a certain temperature range [72]. In 2008, the TSS-CW method was used with Zpex 3Y-TZP, being heated to T1 (1250 °C–1350 °C) at 5 °C/min, held for 1 min, then cooled to T2 (1050 °C–1250 °C) and held between 2 h and 30 h [68]. When compared to conventional sintering under similar conditions, this method showed a slower grain growth rate [68]. It also produced a higher densification at a smaller grain size (110 nm compared to 275 nm), with optimal conditions being the 1300 °C-1050 °C, 30 h cycle [68].

A study performed in 2004 also investigated the TSS-CW method on 3Y-TZP. It used a heat rate of 10 °C/min to reach a T1 of 1500 °C, was held for 5 min, then cooled to a T2 of 1300 °C and held for 10 h [73]. It resulted in a flexural strength of 1078 MPa compared to the 295 MPa achieved using conventional sintering [73]. Grain size at optimal density was also smaller using TSS-CW (560 nm compared to 1050 nm) [73]. The differences in the resulting grain sizes for the studies can be attributed to differing forming methods (pressing vs. injection moulding) and powder particle sizes (75 nm vs. 270 nm) [68,72,73]. Nevertheless, both studies show vast improvement in grain growth rate and grain size achieved using the TSS-CW method, which will produce preferable mechanical and optical properties for the dental prosthetics.

## 5. Conclusions

The use of zirconia in dental ceramics is evidently becoming quite established, with major advancements in the last decade especially on 3Y-TZP. This can be attributed to its capabilities of meeting all key patient satisfaction criteria (comfort, functionality, social aspects, appearance). 3Y-TZP prosthetics are commonly formed and machined from partially sintered blanks, such as those produced by CeramTec, due to increased reliability and less intense machining demands. While there has been extensive research and experimentation on the optimisation of key processes such as pressing and sintering, there was inevitably going to be knowledge gaps for such a newly realised technology. It will be beneficial to CeramTec and to the prosthodontic industry if new and alternative sintering techniques, such as two-step sintering, were investigated for their blanks. Experimentation with two-step sintering has shown positive results in improving mechanical properties. There are also no significant cost increases associated with this method compared to conventional sintering, as similar equipment is utilised for both. The objective of further investigations would be to optimise key parameters such as hardness, flexural strength, and grain growth and size, whilst maintaining the superior aesthetic properties they possess. These can be compared to the results of the prescribed sintering conditions, and to products fully processed from green zirconia powder.

## Conflicts of interest

The authors declare no conflicts of interest.

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